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Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number:

0 336 564 B1

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: **19.05.93** 51 Int. Cl.⁵: **C07C 15/24**

21 Application number: **89302250.9**

22 Date of filing: **07.03.89**

54 **Process for separating methyl derivatives of naphthalene according to crystallization under pressure.**

30 Priority: **07.03.88 JP 51740/88**

43 Date of publication of application:
11.10.89 Bulletin 89/41

45 Publication of the grant of the patent:
19.05.93 Bulletin 93/20

84 Designated Contracting States:
DE FR GB IT NL

56 References cited:
US-A- 3 590 091

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Description

The invention relates to a process for separating 2,6-dimethylnaphthalene in a high purity of more than 98 weight % from a mixture containing this methyl derivative of naphthalene and a process for separating 2-methylnaphthalene in a high purity of more than 98 weight % from a mixture containing this methyl derivative of naphthalene. The dimethylnaphthalene and the methylnaphthalene are abridgedly called hereafter respectively DMN and MN.

2,6-DMN is oxidized and 2-MN is acylated and then oxidized to be naphthalene-2,6-dicarboxylic acid, which is an industrially important material for manufacturing polyester and as a component for a plasticizer. 2,6-DMN and 2-MN are contained in various fractions of petroleum and coal tar as mixtures together with other DMN and MN isomers.

As for separation of 2,6-DMN and 2-MN from such fractions, various processes have been proposed.

For instance, it is well known to those skilled in the art to cool the DMN fraction obtained by concentrating and extracting of petroleum or coal tar material so as to obtain a solid product containing 2,6- and 2,7-DMN, which is then subjected to recrystallization or partial melting in order to separate 2,6-DMN. 2-MN is separated by continuous crystallization or recrystallization of the MN fraction in order to separate 2-MN.

The DMN compounds, however, generally form eutectic mixtures. For instance, 2,6-DMN and 2,7-DMN form a two-component eutectic mixture in the mole ratio of 41.5 : 58.5. 2,6- and 2,3-DMN form a two-component eutectic mixture in the mole ratio of 47.5 : 52.5. Therefore, the conventional process for separating 2,6-DMN of a high purity which relies on the recrystallization method can not attain a high separation yield, since the yield of 2,6-DMN is theoretically decided depending on the material composition.

For instance the fraction of the boiling point of 250 - 270°C obtained by catalytically cracking petroleum contains 8 - 13% of 2,6-DMN and 8 - 13% of 2,7-DMN so that when separating and purifying by cooling, solidifying and recrystallizing or partially melting thereof, the yield for recovering of 2,6-DMN is to be about 30 % at the highest.

It is possible to increase the 2,6-DMN content in the material up to 30% according to the rectification, but it is impossible to considerably change the ratio of 2,6-DMN and 2,7-DMN so that the yield of pure 2,6-DMN can not be raised.

Various fractions from petroleum or coal tar contains 2,6-DMN and 2,7-DMN in the same amount in addition to which various components inclusive of DMN isomers are contained. 2-MN and 1-MN are contained in the concerned fraction in the ratio of 2 : 1. The boiling points of 2,6-DMN and 2,7-DMN as well as of 2-MN and 1-MN are very close respectively to each other so that the eutectic mixture and the solid solution thereof may be formed.

Thus, separation of 2,6-DMN encounters the problems of decreased recovering yield, difficulty of raising the purity and considerably high cost of separation and purification. The same is applied to separation and purification of 2-MN.

In order to solve the problems referred to above, it has been proposed to utilize a process involving crystallization under pressure, which is superior to recrystallization, partial melting and continuous crystallization, in that the apparatus used can be more compact, and it is possible to achieve lower costs, higher yield and higher purity. However, the process is disadvantageous in that impurities in the material are subjected to oxidative polymerization with a relatively small amount of oxygen due to localised superheating under high pressure in the pressure crystallizing apparatus and oxidized polymers mingle with the separated product crystals.

The crystals of 2,6-DMN and 2-MN separated according to this pressure crystallization method are, thus, colored in black and the qualities thereof are considerably deteriorated due to the oxidized polymers of the impurities in the material so that the separated products are commercially less valuable. The method also has a disadvantage in that the discharged liquid can not be reused for the reason referred to above.

SUMMARY OF THE INVENTION

An object of the invention is, thus, to provide a process for separating methyl derivatives of naphthalene from a mixture containing such derivatives without the disadvantages referred to above of the prior art.

It is a particular object to provide a process for separating 2,6-DMN and 2-MN by crystallization under pressure respectively in a high purity of more than 98% by weight without the disadvantages of the prior art referred to above with a lower cost and a higher yield.

The other objects of the invention and advantageous effects attained thereby will be appreciated by those skilled in the art when studying the full explanation of the invention to be given hereafter.

According to the present invention therefore there is provided a process for separating a methyl derivative of naphthalene comprising steps of preliminary treating a starting mixture material containing said derivative in the presence of an acid catalyst at a raised temperature for polymerizing impurities in the material, removing said polymerized impurities from the starting mixture material, and crystallizing under pressure of the material in which the derivative content is increased so as to obtain the methyl derivative of naphthalene in a high purity more than 98% by weight.

The process of the invention is carried out in a preferred embodiment by heating a raw material containing 2,6-DMN or 2-MN in the presence of an acid catalyst to polymerize the impurities in the material, and then distilling the treated material to remove the polymerized impurities and to increase the 2,6-DMN or 2-MN content at least up to 50 weight %, and subsequently, subjecting the treated material to crystallization at a particular temperature and under a particular pressure.

The reason why the 2,6-DMN or 2-MN content is increased to at least 50 weight %, lies in that the yield of the object compound is too low, and also the object compound with the high purity more than 98 weight % is not obtained, in the case that said content is less than 50 weight %.

By removing the impurities in the starting material, the disadvantages caused by utilizing the crystallization under pressure as mentioned above, are removed, thereby obtaining the object compound with the high purity.

DESCRIPTION OF ACCOMPANYING DRAWINGS

Fig. 1 is a graph showing curves of solid-liquid equilibrium in relation to the temperature and pressure for explaining the crystallization under pressure, and

Fig. 2 is a schematic view of the apparatus for carrying out the process according to the invention.

EXPLANATION OF PREFERRED EMBODIMENTS OF THE INVENTION

A fraction of a boiling point of 250 - 270 °C, preferably 257 - 265 °C (for separation of 2,6-DMN) or of 220 - 250 °C, preferably 235 - 245 °C (for separation of 2-MN), obtained by catalytically cracking petroleum, is used as the starting material which contains 2,6-DMN or 2-MN and other isomers thereof. This starting material is not subjected directly to crystallization under pressure but is heated in the presence of an acid catalyst in advance, so as to polymerize some impurities such as aromatic hydrocarbons and other unstable substances containing nitrogen, sulphur or oxygen which are apt to be oxidatively polymerized and difficult to be removed e.g. by a simple distillation, and is then distilled so as to increase the 2,6-DMN or 2-MN content to be at least 50% by weight, preferably higher than 70% by weight.

The material thus treated in advance is then subjected to crystallization under pressure. Otherwise the yield of the objective compound is poor and a high purification of more than 98% can not be expected.

As for raising the 2,6-DMN or 2-MN content in the concerned fraction itself, the cooling crystallization method and the zeolite method are already in public knowledge e.g. by U.S. Patent 3,590,091 and JP-B 27,578/1974. According to the former, the concerned cracking fraction is crystallized at a temperature of -15 - +5 °C (for 2,6-DMN) or -40 ° - +10 °C (for 2-MN). According to the latter, the DMN fraction is treated at 80 - 100 °C, with SV 1g/g/hr in the presence of zeolite Na-Y, and as occasion demands further subjected to crystallization at a temperature of -35 - +10 °C. These treatments, however, are practically not only troublesome but also difficult to sufficiently raise the concentration of 2,6-DMN or 2-MN in the material mixture so that even if the treated material is subjected to the crystallization under pressure, the defects referred to above can not be overcome.

As for the above mentioned acid catalyst used for treating the raw material prior to the pressure crystallization this may be any of the acid catalysts such as sulfuric acid and phosphoric acid as are used e.g. for olefin polymerization. Solid acid catalyst such as silica, alumina, silica-alumina, chromia, titania, zirconia, chromia-alumina, clay, bauxite, zeolite, activated carbon and activated clay also may be used. The surface acidity of the catalyst is sufficient to be in such a degree as to discolor benzeneazodiphenylamine. Suitable properties of the solid catalyst are 100 - 500 m²/g, preferably 150 - 300 m²/g surface area, 30 - 300 Å, preferably 50 - 100 Å average porous diameter, 0.1 - 1.0 cc/g porous volume and 10 - 100 mesh, preferably 30 - 60 mesh particle dimension. Particularly desirable acid catalyst for the process of the invention is an activated clay comprising a main content of 2 : 1 type layer structure such as montmorillonite.

The treatment is carried out at a temperature preferably in the range of 120 – 200 °C. When the temperature is higher than 220 °C, disproportionation, isomerization, demethylation and other undesirable side reactions of aromatic compounds contained in the treated mixture material occur. The treatment is done under such a pressure as to keep the material in a liquid phase in relation to the temperature, generally at the atmospheric. A liquid phase space velocity (LHSV) of the reaction column is generally 0.1 – 6 Hr⁻¹, and preferably 0.2 – 2 Hr⁻¹.

The starting material to be treated according to the invention prior to the crystallization under pressure comprises aromatic compounds and other unstable substances having nitrogen, sulphur or oxygen which are readily oxidized or oxidatively polymerized with a small amount of oxygen at the treatment temperature so as to discolor the product or form undesirable sludge as referred to above.

According to the treatment referred to above such impurities are polymerized to be readily removed from the material by distillation and consequently raise the DMN or MN content therein up to 70% by weight.

The treated material is then subjected to the crystallization under pressure, according to which 2,6-DMN or 2-MN in the liquid mixture material is solidified under a pressure higher than the solid-liquid modification pressure thereof in a sealed vessel so as to exclude the liquid phase from the formed solid-liquid co-existing system and compress the solid phase to "squeeze out" the remaining liquid among solid particles and conglomerate the particles.

Now expressing a concentration of impurities in the remaining liquid as X₂ (molar concentration), a treatment temperature as T (absolute), a solid (crystal)-liquid equilibrium pressure as P₁ (kg/cm²), a solid-liquid modification pressure of pure substance as P₀ (kg/cm²) and a difference between said P₁ and P₀ as ΔP (kg/cm²), the following relation is established when X₂ is of a small value;

$$\Delta P = \frac{RT}{\Delta V} X_2$$

in which R is a gas constant and ΔV means a volume change per mole caused by solidification (generally negative value).

Further expressing a statistically average contact pressure of crystalline interface as P_S, a solid-liquid equilibrium pressure of the residual liquid with impurity concentration X₂ as P₀ + ΔP and a pressure of excluding the residual liquid as P_L, the relation of P₀ < P_L < P₀ + ΔP < P_S is the best for attaining the purpose. As P_L nears close to P₀ + ΔP, the recovered solid amount is increased but the purifying effect is lowered. When P_L nears to P₀, the solid recovering efficiency is a little lowered but the purification can be efficiently made. It is possible, thus, to obtain the high purity of solid in a higher yield only by removing a relatively small amount of the residual liquid, when nearing P_L from P₀ + ΔP closer to P₀ depending on the concentration and excluded amount of the residual liquid.

In reference to Fig. 1 a curve gradient of solid-liquid equilibrium dP₀/dT is generally larger than zero. When an absolutely pure substance in which the impurity concentration X₂ = 0 is in solid-liquid equilibrium state at a temperature T under a pressure P₀, the solid-liquid equilibrium pressure in case of the substance of impurity concentration X₂ comes to P₀ + ΔP. When setting a residual liquid excluding pressure at P_L, the solid in the vicinity of the liquid of impurity concentration X₂ is melted so as to attain the solid-liquid equilibrium to be made purer. The then statistically average pressure of crystalline interface P_S is far higher than the pressures referred to above so as to affect a pressure on the crystal particles, whereby the residual liquid is "squeezed out".

When the temperature is lowered down to T' which is caused by melting some amount of crystals as a result of setting the excluding pressure at P_L, it is possible to adjust the excluding pressure with considering the then pressure P₀', newly as P₀ or to understand it as a variable to return to the initial value as a result of the temperature recovery.

The invention will be more definitely explained in reference to Fig. 2 in which the apparatus for crystallizing under pressure according to the invention, is illustrated.

In the case that 2,6-DMN is used for the starting material, the 2,6-DMN contained in 250 – 270 °C fraction obtained by catalytically cracking petroleum is preliminarily concentrated (by thermally treating with the acid catalyst and distilling) to obtain a mixture of at least 50 weight %, preferably 70 weight % of 2,6-DMN and another DMN isomer, and then said mixture is preliminarily adjusted to a temperature of 80 – 105 °C to form a slurry containing the crystal of 2,6-DMN and the isomer thereof.

In the case that 2-MN is used for the starting material, the 2-MN contained in 220 - 250 °C fraction obtained by catalytically cracking petroleum is preliminarily concentrated to obtain a mixture of at least 50 weight %, preferably 70 weight % of 2-MN and an another MN isomer, and then, said mixture is preliminarily adjusted to a temperature of 10 - 35 °C to form a slurry containing the crystal of 2-MN and the isomer thereof. Each said mixture is fed from a material tank 14 to a primary crystallization zone 2 through a conduit 3 by means of a motor driven pump 4 so as to form seed crystals therein. Otherwise not only higher pressure is necessitated for causing primary crystallization but also ultrafine crystals are formed under a supersaturated condition due to the rapid pressurization, which may lead to separation difficulty. Owing to formation of crystalline seeds, the supersaturated condition is not caused so that crystal growth can be started immediately upon a pressurization.

The material containing crystalline seeds of 2,6-DMN or 2-MN is then fed to a pressure vessel 5 through a conduit 6 provided with a valve 7 by means of a pump 8.

The pressure vessel 5 comprises a vertically movable piston 9 which is actuated by a hydraulic unit 10 so as to define a chamber 11 for crystallization under pressure between the free end of the piston 9 and the bottom wall of the chamber 11 in which pressure may be raised by lowering the piston down.

The piston is preferably arranged with a conduit for overflow provided with a valve 13 and opened at the piston free end so that when the supplied material is filled in the chamber 11 to flow into the conduit 12, the overflow is detected to close the valves 7, 13 and the piston 9 is lowered to raise the pressure in the chamber.

Thereby the material in the chamber 11 is made in the solid-liquid coexisting state as referred to above. The resulting 2,6-DMN or 2-MN in solid state is already of a high purity. As the solidification thereof is progressed, the temperature is raised, but it is generally preferable not to cool the system.

The temperature after the pressure is raised adiabatically up to 500 - 2500 kgf/cm², at which the solid-liquid separation is started, affects on the purity and yield of the product. Thus, the temperature of the material to be supplied is controlled at 80 - 105 °C in case of 1,2-DMN and at 10 - 35 °C in case of 2-MN as referred to above with taking into consideration, in advance, of a specific heat, a solidification latent heat and so on of the mixture material so that a desired temperature can be resultingly held.

Then, a valve 14 is opened for discharging the liquid content in the crystallizing chamber 11 through a conduit via a decompressor 16 into a waste liquid tank 17, with keeping the pressure in the chamber 11 by lowering the piston 9 down. The crystal particles of 2,6-DMN or 2-MN are thus pressed so as to "squeeze out" the liquid contents remained thereamong to be exhausted out of the chamber 11 into the tank 17.

As the piston 9 is further lowered, the crystal particles are further pressed to form a large mass in the form of the decreased volume of chamber 11. When the liquid content in the solid phase is almost completely excluded and discharged out of the chamber, the liquid phase pressure is correspondingly decreased so that crystalline surfaces are partially melted so as to increase the degree of purification by virtue of the so-called "sweating effect". Thereby the purity of the separated 2,6-DMN or 2-MN product reaches at 98 % or more.

Then, the piston is raised up to be in the initial position and the product is taken out by opening the lid provided in the bottom wall of the pressure vessel 5.

The invention will be explained in more detail in reference to following Examples.

Example 1

The starting material comprising 67 weight % of 2,6-DMN, other DMN isomers inclusive of 9 weight % of 2,7-DMN and a small amount of impurities were preliminarily treated in the presence of the marketed activated clay as an acid catalyst. The properties thereof were as follows;

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(1) Particle dimension	30 – 60 mesh
(2) Bulk density	0.63
(3) Specific surface area	281 m ² /g
(4) Porous volume	0.39 ml/g
(5) Average porous diameter	55 Å
(6) Free acid	2.6 mg KOH/g
(7) Chemical composition	(wt %)
SiO ₂	76.0
Al ₂ O ₃	10.3
Fe ₂ O ₃	1.7
CaO	< 0.1
MgO	1.5
Ignition loss	10.0

The starting material was passed through the activated clay at a temperature of 160 °C with 0.5 Hr⁻¹ of LHSV and then subjected to distillation for removing polymerized impurities so as to obtain colorless oily material.

20 This mixture material was continuously heated at 200 °C for 200 hours in air in a sealed glass tube to recognize almost no change from the initial state.

The mixture material was subjected to the preliminary crystallization so as to contain crystalline seeds of 2,6 – DMN. The material in the slurry state was fed to a pressure vessel of the hydraulic piston – cylinder structure to be subjected to an adiabatic pressure of 1500 kgf/cm². Then the liquid phase in the pressure vessel was discharged therefrom with keeping the pressure and 2,6 – DMN crystals pressed until the liquid phase pressure fell down to 200 kgf/cm².

Obtained crystalline 2,6 – DMN was not colored and had a purity of about 98 %.

Example 2

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The starting material comprising 65 weight % of 2 – MN, 7 weight % of 1 – MN and a small amount of impurities were preliminarily treated similar to Example 1.

The obtained oily colorless material was continuously heated similar thereto to find no substantial change.

35 The material was subjected to the crystallization under pressure like as in Example 1 except the temperature of the supplied material was controlled to be of 5 °C.

Obtained crystalline 2 – MN was not colored and had a purity of about 98 %.

The residual mother liquors in Examples 1 and 2 were cyclically used in the subsequently repeated treatment.

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Claims

1. A process for separating a methyl derivative of naphthalene comprising steps of preliminarily treating a starting mixture material containing said derivative in the presence of an acid catalyst at a raised temperature for polymerizing impurities in the material, removing said polymerized impurities from the starting mixture material, and crystallizing under pressure of the material in which the derivative content is increased so as to obtain the methyl derivative of naphthalene in a high purity more than 98 % by weight.

50 2. The process as set forth in Claim 1, in which the 2,6 – dimethyl naphthalene content in the preliminarily treated mixture material, which is to be subjected to the crystallization under pressure, is raised up to at least 50 % by weight.

55 3. The process as set forth in Claim 1, in which the 2 – methyl naphthalene content in the preliminarily treated mixture material, which is to be subjected to the crystallization under pressure, is raised up to at least 50 % by weight.

4. The process as set forth in Claim 2, in which the preliminarily treated mixture material containing 2,6-dimethyl naphthalene, of which temperature is controlled to be of 80 - 105 °C, is subjected to the crystallization under a pressure of 500 - 2500 kgf/cm².
5. The process as set forth in Claim 3, in which the preliminarily treated mixture material containing 2-methyl naphthalene, of which temperature is controlled to be of 10 - 35 °C, is subjected to the crystallization under a pressure of 500 - 2500 kgf/cm².
6. The process as set forth in any of Claims 1 - 5, in which the starting mixture material is preliminarily treated in the presence of the acid catalyst at a raised temperature up to 220 °C at the highest and with a liquid phase space velocity of 0.1 - 6 Hr⁻¹.
7. The process as set forth in Claim 6, in which the starting mixture material containing dimethyl naphthalenes is a fraction with b.p. of 250 - 270 °C obtained by catalytically cracking petroleum and subjected to the preliminary treatment in the presence of the acidic catalyst at a temperature of 120 - 200 °C and with a liquid phase space velocity of 0.2 - 2Hr⁻¹ and then to a fractional distillation.
8. The process as set forth in Claim 6, in which the starting mixture material containing methyl naphthalenes is a fraction with b.p. of 220 - 250 °C obtained by catalytically cracking petroleum and subjected to the preliminary treatment in the presence of the acidic catalyst at a temperature fo 120 - 200 °C and with a liquid phase space velocity of 0.2 - 2 Hr⁻¹ and then to a fractional distillation.
9. The process as set forth in any of Claims 1 - 8, in which the acid catalyst is a solid catalyst and a liquid catalyst used generally for the olefin polymerization.
10. The process as set forth in Claim 9, in which the liquid catalyst is sulfuric acid or phosphoric acid.
11. The process as set forth in claim 9, in which the solid catalyst is silica, alumina, silica-alumina, chromia, titania, zirconia, chromia-alumina, clay, bauxite, zeolite, activated carbon or activated clay.
12. The process as set forth in Claim 9, in which the surface acidity of the acid catalyst is in such a degree as to discolor benzeneazodiphenylamine.
13. The process as set forth in Claim 9, in which the solid acid catalyst has a surface area of 100 - 500 m²/g, an average porous diameter of 30 - 300Å, a porous volume of 0.1 - 1.0 cc/g and a particle dimension of 10 - 100 mesh.
14. The process as set forth in Claim 11, in which activated clay catalyst is of montmorillonite system having 2 : 1 type layer structure.

Patentansprüche

1. Verfahren zum Abtrennen eines Methylderivates von Naphthalin, umfassend Stufen des vorausgehen - den Behandeln eines dieses Derivat enthaltenden Ausgangsmischungs - Materials in Gegenwart eines sauren Katalysators bei einer erhöhten Temperatur zum Polymerisieren von Verunreinigungen in dem Material, Entfernen dieser polymerisierten Verunreinigungen aus dem Ausgangsmischungs - Material und Kristallisieren des Materials, in welchem der Gehalt des Derivates angestiegen ist, unter Druck, wodurch das Methylderivat von Naphthalin in einer Reinheit von mehr als 98 Gewichts - % erhalten wird.
2. Verfahren nach Anspruch 1, worin der 2,6-Dimethylnaphthalingehalt im zuvor behandelten Mischungs - Material, das der Kristallisation unter Druck unterworfen werden soll, auf mindestens 50 Gewichts - % angehoben wird.
3. Verfahren nach Anspruch 1, worin der 2-Methylnaphthalingehalt im zuvor behandelten Mischungs - Material, das der Kristallisation unter Druck unterworfen werden soll, auf mindestens 50 Gewichts - % angehoben wird.

4. Verfahren nach Anspruch 2, worin das zuvor behandelte, 2,6-Dimethylnaphthalin enthaltende Mischungs-Material, dessen Temperatur auf einen Stand von 80 - 105 °C eingeregelt wird, der Kristallisation unter einem Druck von 500 - 2500 kgf/cm² unterworfen wird.
5. Verfahren nach Anspruch 3, worin das zuvor behandelte, 2-Methylnaphthalin enthaltende Mischungs-Material, dessen Temperatur auf einen Stand von 10 - 35 °C eingeregelt wird, der Kristallisation unter einem Druck von 500 - 2500 kgf/cm² unterworfen wird.
6. Verfahren nach einem beliebigen der Ansprüche 1 - 5, worin das Ausgangsmischungs-Material zuvor in Gegenwart des sauren Katalysators bei einer bis auf maximal 220 °C erhöhten Temperatur und mit einer Raumgeschwindigkeit der flüssigen Phase von 0,1 - 6 h⁻¹ behandelt wird.
7. Verfahren nach Anspruch 6, worin das Dimethylnaphthaline enthaltende Ausgangsmischungs-Material eine Fraktion mit einem Siedep. von 250 - 270 °C ist, die durch katalytisches Cracken von Erdöl erhalten wurde und dem vorausgehenden Behandeln in Gegenwart des sauren Katalysators bei einer Temperatur von 120 - 200 °C und mit einer Raumgeschwindigkeit der flüssigen Phase von 0,2 - 2 h⁻¹ und dann einer fraktionierten Destillation unterworfen wird.
8. Verfahren nach Anspruch 6, worin das Methylnaphthaline enthaltende Ausgangsmischungs-Material eine Fraktion mit einem Siedep. von 220 - 250 °C ist, die durch katalytisches Cracken von Erdöl erhalten wurde und dem vorausgehenden Behandeln in Gegenwart des sauren Katalysators bei einer Temperatur von 120 - 200 °C und mit einer Raumgeschwindigkeit der flüssigen Phase von 0,2 - 2 h⁻¹ und dann einer fraktionierten Destillation unterworfen wird.
9. Verfahren nach einem beliebigen der Ansprüche 1 bis 8, worin der saure Katalysator ein fester Katalysator und eine flüssiger Katalysator ist, welche üblicherweise für die Olefinpolymerisierung verwendet werden.
10. Verfahren nach Anspruch 9, worin der flüssige Katalysator Schwefelsäure oder Phosphorsäure ist.
11. Verfahren nach Anspruch 9, worin der feste Katalysator Siliciumdioxid, Aluminiumoxid, Siliciumdioxid - Aluminiumoxid, Chromoxid, Titandioxid, Zirkoniumdioxid, Chromoxid - Aluminiumoxid, Tonerde, Bauxit, Zeolith, Aktivkohle oder aktivierte Tonerde ist.
12. Verfahren nach Anspruch 9, worin der Säuregrad der Oberfläche des sauren Katalysators eine solche Stärke aufweist, daß Benzolazodiphenylamin entfärbt wird.
13. Verfahren nach Anspruch 9, worin der feste saure Katalysator eine Oberfläche von 100 - 500 m²/g, einen durchschnittlichen Porendurchmesser von 30 - 300 Angström, ein Porenvolumen von 0,1 - 1,0 ccm/g und eine Teilchengröße von 10 - 100 mesh aufweist.
14. Verfahren nach Anspruch 11, worin der Katalysator aus aktivierter Tonerde dem Montmorillonit-System mit Schichtstruktur vom 2 : 1 Typ angehört.

45 **Revendications**

1. Procédé de séparation d'un dérivé méthylique du naphthalène, comprenant les stades de traitement préliminaire de la matière formée du mélange de départ et contenant le dérivé en la présence d'un catalyseur acide à une température élevée pour polymériser les impuretés dans la matière, d'élimination des impuretés polymérisées de la matière formant le mélange de départ et de cristallisation sous pression de la matière dans lequel la teneur en le dérivé est augmentée de manière à obtenir le dérivé méthylique du naphthalène en une grande pureté, supérieure à 98 % en poids.
2. Procédé suivant la revendication 1, dans lequel la teneur en 2,6-diméthyl-naphthalène de la matière formant le mélange traité préalablement, qui est soumise à la cristallisation sous pression, est portée à au moins 50 % en poids.

3. Procédé suivant la revendication 1, dans lequel la teneur en 2-méthylnaphtalène de la matière formant le mélange traité préalablement, qui est soumis à la cristallisation sous pression, est portée à au moins 50 % en poids.
- 5 4. Procédé suivant la revendication 2, dans lequel la matière formant le mélange traité préalablement et contenant du 2,6-diméthylnaphtalène, dont la température est réglée entre 80 et 105 °C, est soumise à la cristallisation sous une pression de 500 à 250 kgf/cm².
- 10 5. Procédé suivant la revendication 3, dans lequel la matière formant le mélange traité préalablement et contenant du 2-méthylnaphtalène, dont la température est réglée entre 10 et 35 °C est soumise à la cristallisation sous une pression de 500 à 2500 kgf/cm².
- 15 6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel la matière formant le mélange de départ est traitée préalablement en la présence d'un catalyseur acide à une température portée à 220 °C au plus et avec une vitesse spatiale de la phase liquide de 0,1 à 6 H⁻¹.
- 20 7. Procédé suivant la revendication 6, dans lequel la matière formant le mélange de départ et contenant des diméthylnaphtalènes est une fraction d'un point d'ébullition compris entre 250 et 270 °C, obtenus en craquant catalytiquement du pétrole et est soumise au traitement préalable en la présence du catalyseur acide à une température de 120 à 200 °C et avec une vitesse spatiale de la phase liquide de 0,2 à 2H⁻¹, puis à une distillation fractionnée.
- 25 8. Procédé suivant la revendication 6, dans lequel la matière formant le mélange de départ et contenant des méthylnaphtalènes est une fraction ayant un point d'ébullition compris entre 220 et 250 °C, obtenue en craquant catalytiquement du pétrole, et est soumise au traitement préalable en la présence du catalyseur acide à une température de 120 à 200 °C et avec une vitesse spatiale de la phase liquide de 0,2 à 2H⁻¹, puis à une distillation fractionnée.
- 30 9. Procédé suivant l'une quelconque des revendications 1 à 8, dans lequel le catalyseur acide est un catalyseur solide et un catalyseur liquide utilisé, en général, pour la polymérisation des oléfines.
- 35 10. Procédé suivant la revendication 9, dans lequel le catalyseur liquide est l'acide sulfurique ou l'acide phosphorique.
- 40 11. Procédé suivant la revendication 9, dans lequel le catalyseur solide est de la silice, de l'alumine, de la silice-alumine, de l'oxyde de chrome, de l'oxyde de titane, de la zircone, de l'oxyde de chrome-alumine, de l'argile, de la bauxite, de la zéolite, du charbon actif ou de la terre activée.
- 45 12. Procédé suivant la revendication 9, dans lequel l'acidité superficielle du catalyseur acide est telle qu'elle fait virer la benzèneazodiphénylamine.
- 50 13. Procédé suivant la revendication 9, dans lequel le catalyseur acide solide a une surface spécifique comprise entre 100 et 500 m²/g, un diamètre moyen de pore compris entre 30 et 300 Å, un volume de pores compris entre 0,1 et 1,0 cm³/g et une granulométrie comprise entre 2 et 0,15 mm.
- 55 14. Procédé suivant la revendication 11, dans lequel le catalyseur à base de terre activée est un système à base de montmorillonite ayant une structure stratifiée de type 2:1.

Fig.1

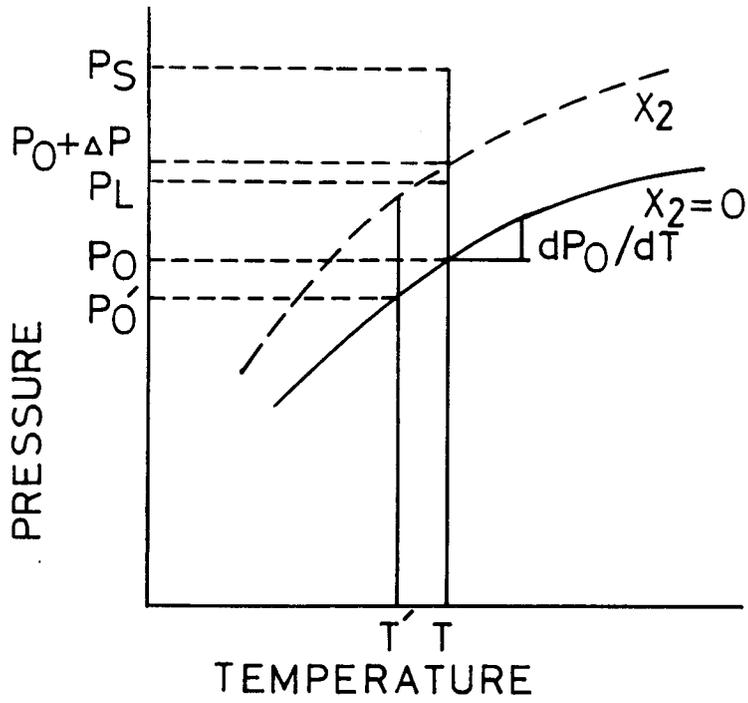


Fig.2

